SEMI-ANNUAL STATUS REPORT #5

For the Period

1 July 1968 to 30 June 1969

DEFECT PRODUCTION IN SINGLE CRYSTALS RESULTING FROM ION BOMBARDMENT

by

Lawrence B. Shaffer

Prepared for

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

29 August 1969

GRANT NGR 36-019-001

X RAY PHYSICS LABORATORY
Hiram College
Hiram, Ohio 44234

SEMI-ANNUAL STATUS REPORT #5

For the Period

1 July 1968 to 30 June 1969

DEFECT PRODUCTION IN SINGLE CRYSTALS RESULTING FROM ION BOMBARDMENT

by

Lawrence B. Shaffer

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

LEWIS RESEARCH CENTER

Cleveland, Ohio

29 August 1969

GRANT NGR 36-019-001

X RAY PHYSICS LABORATORY

Hiram College

Hiram, Ohio 44234

TABLE OF CONTENTS

LIST OF FIGURES

I INTRODUCTION AND SUMMARY

Contained in this report is a summary of the progress made during the time period from July, 1968 through June, 1969 on the work supported by the National Aeronautics and Space Administration to investigate the damage produced on the surface of metal single crystals during ion bombardment using x-ray methods. This report covers two semi-annual periods since equipment delays prevented adequate progress during the period July through December, 1968 to justify a report.

II SINGLE CRYSTAL DAMAGE STUDIES

Ultra High Vacuum System

The vacuum system as supplied by Varian[1] has certain deficiencies which are described in a previous report.[2] The primary problem is that the vacuum specification in the x-ray chamber has not and will not be met even with the addition of the 15 l/S pump. The tests on the rotary feedthrough will be described below. Thus due to the system deficiencies and the nine month shipping delay Hiram College was finally successful in a renegotiation of the system price. The system was paid for on February 11, 1969.

Unfortunately the vacuum system has not provided the only equipment delay. As described in previous reports[3] the vacuum leak in the ion gun became more serious and finally the ion gun needed extensive repair. One of the electrical feedthroughs in an octal feedthrough developed a leak and many attempts to repair it using Torr Seal[4] were unsuccessful necessitating replacement of the complete octal feedthrough. This repair work[5] was done at NASA Lewis Research Center and took six months primarily due to slow delivery of the replacement octal feedthrough. After this repair work the ion gun was again mounted on the system on January 2, 1969 and subsequently another leak was discovered, this time around the leak tube.

Figure one shows the octal socket and the leak tube feedthrough. This leak again could not be repaired using Torr Seal at the leak tube feedthrough which was located in a recessed hole. The ion gun was dismantled and evidently the leak tube feedthrough had developed a leak previously as it was sealed with soft solder. After thoroughly cleaning the part to be soldered (both were stainless steel) the feedthrough was repaired and the ion gun was mounted on the system for a vacuum leak test. With the ion gun mounted on the system the base pressure is 5×10^{-9} Torr with no further evidence of leaks. This pressure will be adequate to proceed with the bombardment study. The ion gun was placed back into service April 25, 1969.

Since April the gun has operated satisfactorily for approximately 69 hours of sputtering time. The procedure used to obtain the discharge in the ion gun is outlined in Table 1. The three hour warm up on the magnetic field coil is necessary to establish thermal and vacuum equilibrium conditions; otherwise continuous adjustments to the coil are required.

TABLE I

Turn up Procedure for Ion Gun

1. Outgas magnetic field coil (@ 8A) and filament (@ 12A) for 3 hours prior to run.
2. Set anode voltage to 60 V.
3. Adjust leak rate of argon to $2\text{-}3 \times 10^{-6}$ Torr.
4. Turn on high voltage power supply to 900 V for screen voltage.
5. Set acceleration voltage to 760 V.
6. Decrease magnetic field current to about 4 A to obtain discharge.
7. Then optimize the discharge by adjusting filament, magnetic field current, screen voltage, and leak rate.

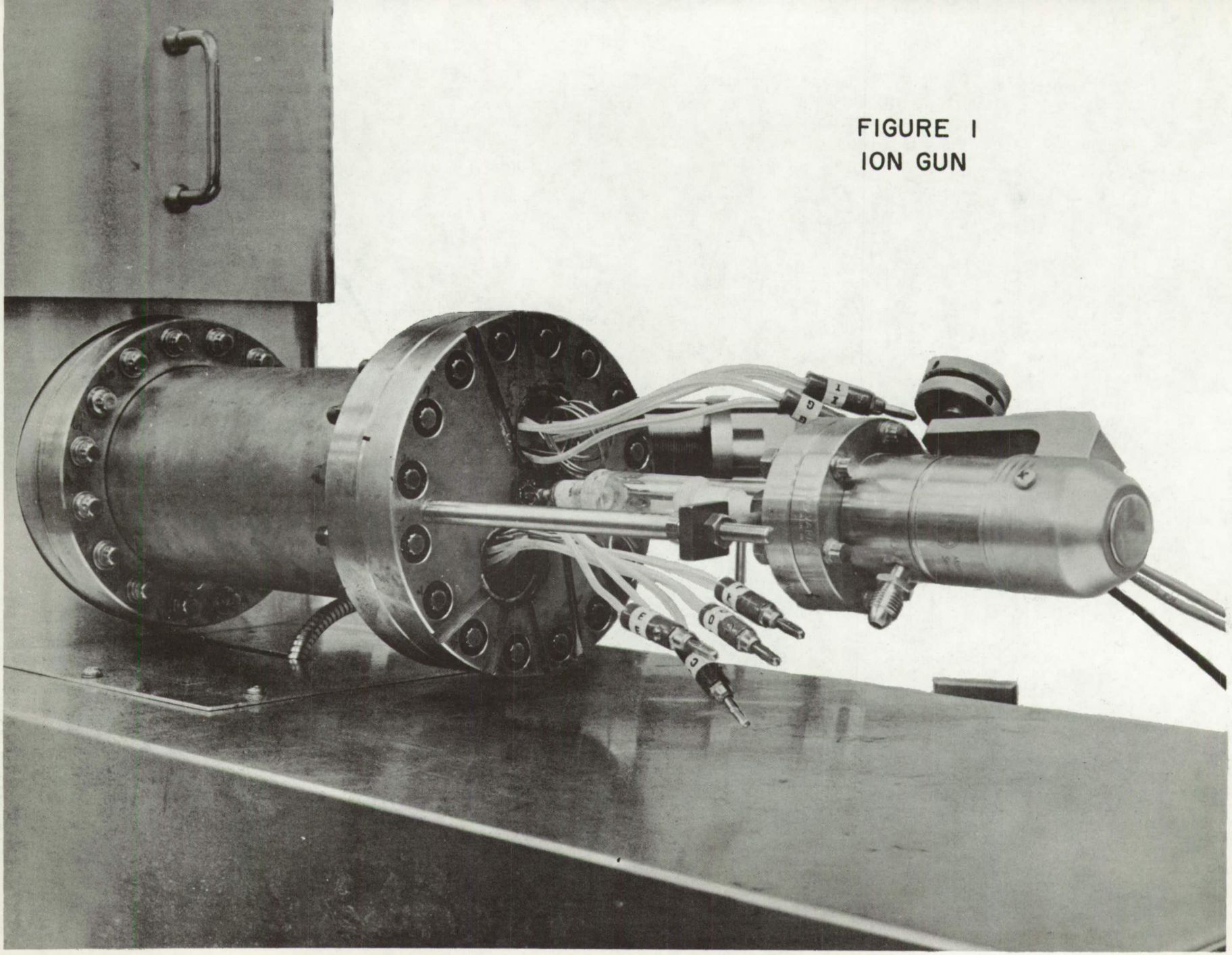


FIGURE I
ION GUN

Some typical operating parameters are filament current, 9.6 A; screen voltage, 800 V; acceleration electrode voltage, 760 V; magnetic field current, 5.2 A; anode current, 390 mA; anode voltage, 60 V; beam current, .48 mA; and crystal current, 125 μA. Figure 2 shows a schematic of the ion gun with all the parameter meters listed above. A Heathkit[5] strip chart recorder is used to continuously monitor the ion beam reaching the crystal. A full scale reading of 125 μA is obtained using a 2 KΩ resistor in parallel with the recorder input. The total beam exposure on the crystal is found by adding up the currents at 1 minute intervals and expressing the result in ion current x time or Coulombs. The crystal beam current stability depends critically upon the pressure range, filament current, and magnetic field current. Fluctuations from 110 μA to 125 μA are not uncommon.

The Varian ion pump apparently develops an "argon instability" in the pressure range around 5×10^{-6} Torr and begins a pressure cycling up and down which usually results in the pump shutting off, i.e. the pressure rising above 1×10^{-4}, unless the argon leak rate is reduced. This cycling usually lasts from 5 to 30 minutes before shutdown occurs. Of course this instability causes problems with the ion beam. Attempts to hold the pressure using only the TSP, i.e. turning off the ion pump have not been successful. If the pressure is kept below 5×10^{-6} Torr, the pump instability usually does not occur.

The Argon gas is of a research grade purchased from Air Products and Chemicals, Inc.[6] The specifications for the gas are listed in Table 2. The gas is delivered to the leak valve[7] at 2-3 psig.

During the delay with the ion gun repair, work proceeded on checking out the rotary feedthrough in the x-ray vacuum chamber and determining a good annealing geometry in the x-ray chamber. The rotary feedthrough test will be described in the next section along with the interface unit test on the double crystal spectrometer. The annealing circuit is shown in Figure 3. For these tests a copper single crystal[8] was mounted on the sample holder. This crystal was 1 inch in diameter and 1/4 inch thick. Thus an indirect heating method (electron bombardment) was used. At 1800 V and 50 mA the annealing temperature of 700°C

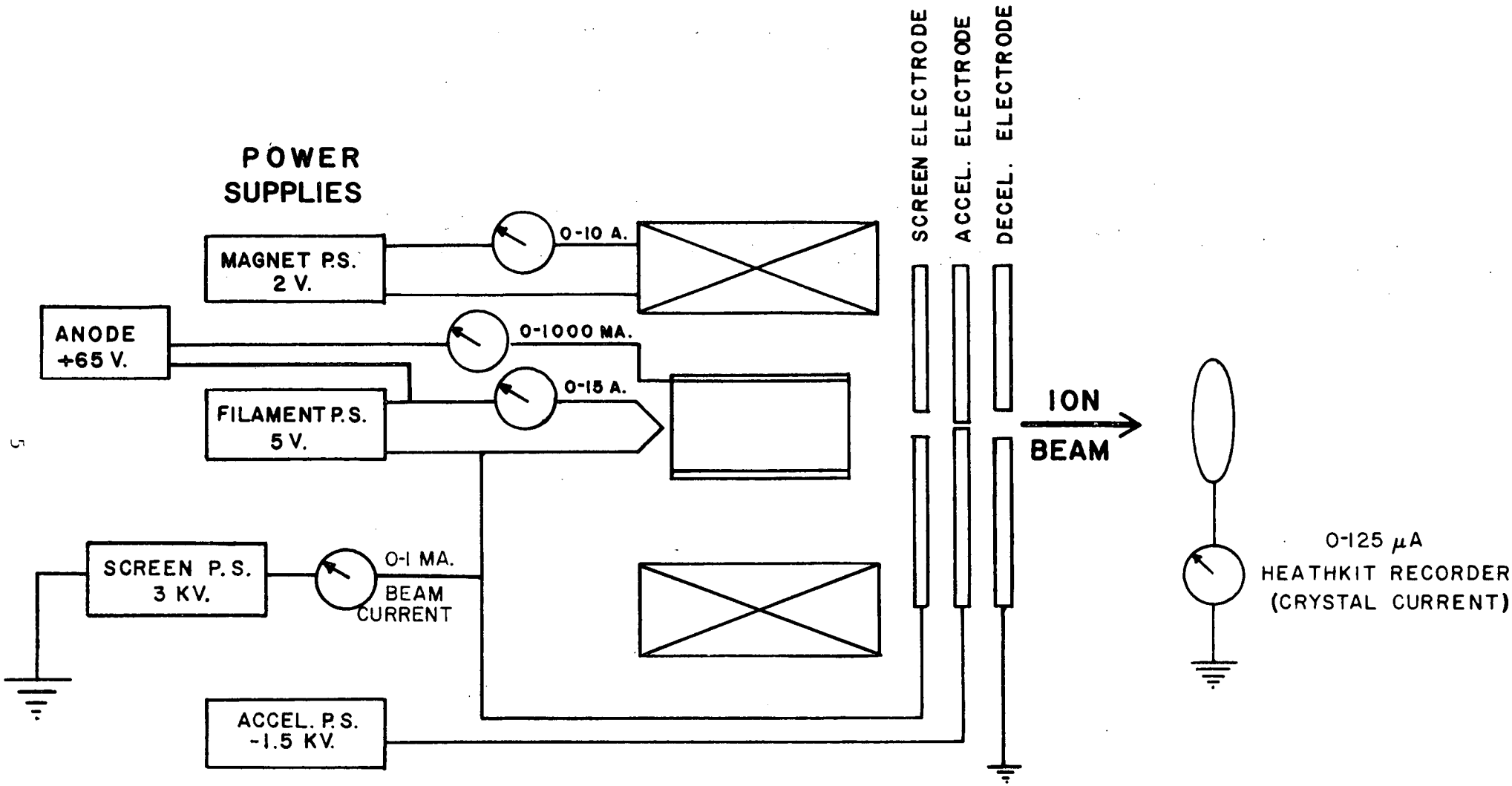


FIGURE 2

ION GUN SCHEMATIC

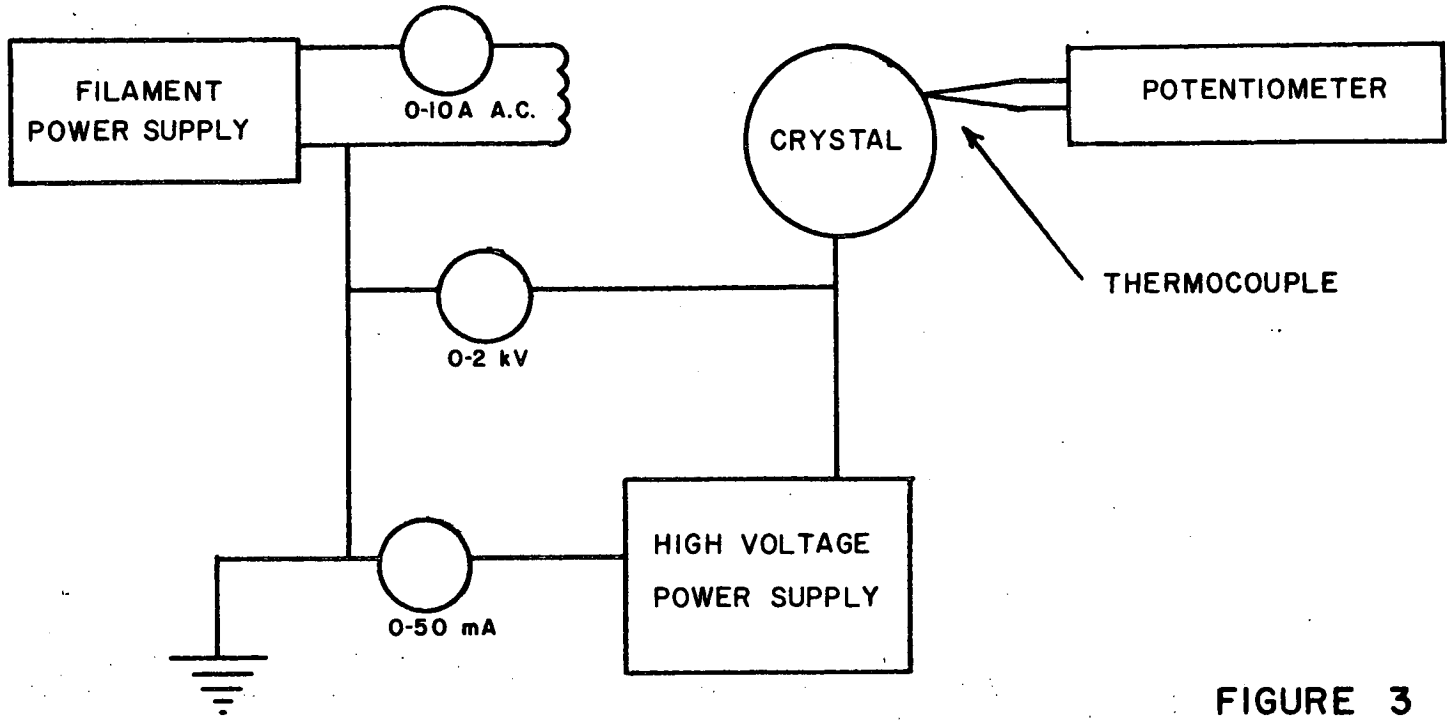


FIGURE 3

ELECTRON BOMBARDMENT

ANNEALING CIRCUIT

was reached in about five minutes with the vacuum staying at 1×10^{-7} Torr. The x-ray chamber geometry and feedthrough has been described in detail previously.[9] Unfortunately during the several operations of bolting and unbolting the 8 inch flange on the x-ray chamber a small leak developed in the weld of the Beryllium window to the chamber walls. So far the leak has been repairable using Torr Seal.

TABLE 2

Analysis of Argon Gas

COMPONENT	AMOUNT	
Oxygen	0.5	Molar ppm
Nitrogen	1.0	Molar ppm
Hydrogen	<1.0	Molar ppm
Carbon Dioxide	<0.5	Molar ppm
Carbon Monoxide	<1.0	Molar ppm
Nitrous Oxide	<0.1	Molar ppm
Methane	<0.5	Molar ppm
Acetylene	<0.05	Molar ppm
Total Hydrocarbons	<1.0	Molar ppm
Water	0.15	Molar ppm
Water	-125°F	Dew Point

Double Crystal Spectrometer

The high voltage power supply for the x-ray tube on the double crystal spectometer as described previously[10] could not be modified to provide satisfactory current regulation. The original control unit was replaced with a solid state version with no significant improvement. The use of the power supply designed for the rotating anode x-ray tube[11] was also unsatisfactory primarily due to high voltage cable connections. After a minor fire with this

arrangement it was decided to purchase a new power supply. The new power supply[12] was installed May 23, 1969 and, after installing a custom high voltage connection, has operated satisfactorily. The cost of this new unit was shared with the college since although the power supply was necessary for the x-ray work, some of the x-ray cameras and attachments will be used in the instructional program of Hiram College.

During the period from August to November, 1968, attempts were made to obtain a double crystal topograph.[13] Although several types of film and long exposure periods (up to 48 hours) were used these attempts were unsuccessful. The positioning of the film in the x-ray beam was also a problem. Additional work will be performed on this problem.

The check out tests for the rotary feedthrough in the x-ray chamber and the interface unit[14] for mounting the x-ray chamber on the double crystal spectrometer were performed in December, 1969. These tests consisted of determining the precision of the rotary feedthrough resettability after an 180° rotation and determining the precision of repositioning the x-ray chamber on the interface unit. To position the x-ray chamber on the double crystal spectrometer so that the quartz crystal was in proper x-ray alignment it was necessary to remove the 8 l/s ion pump, the viewport, and the $1\frac{3}{16}$ straight through valve. Then by mounting a mirror on the face of the crystal so that it extended beyond one end of the crystal it was possible to use a Gauss eyepiece and telescope to adjust the crystal orientation quite closely to the x-ray position. The translation adjustment was made using a dial gauge contacting the mirror. Then the mirror was removed and the final orientation was determined using x-rays. Once the peak position was found and the appropriate tilt adjustments[15] were made the chamber was removed and replaced a total of seven times. The change in the position of the peak of the quartz (200) rocking curve was less than ± 2 seconds of arc. The rotary feedthrough was then tested by rotating the crystal through 180° and then back against the stop a total of seven times. The test performed with the crystal in air indicated a precision of ± 11.5 seconds of arc and with the chamber

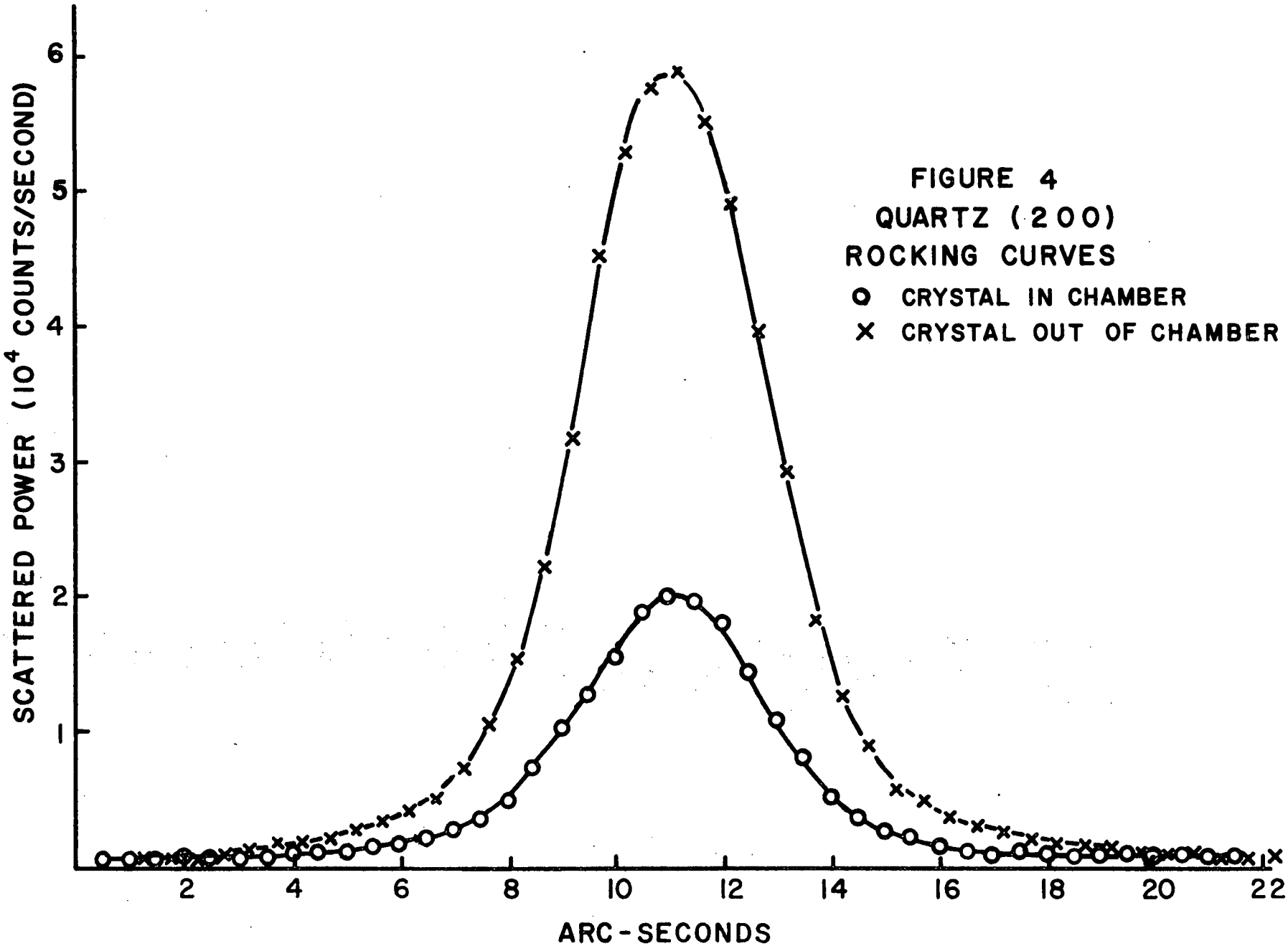
evacuated the resettability was ± 8 seconds. With the chamber reassembled for evacuation a counterweight of 6 kg located about 16 inches from the chamber was necessary. Thus the design of both the rotary feedthrough and the interface unit appears to be within the original specifications.

The quartz crystal was used in the chamber for the above checkout since it has an extremely narrow rocking curve and thus was quite sensitive to small changes in the mechanical mounting and crystal rotation. Figure 4 shows a quartz (200) rocking curve for the crystal both in and out of the chamber to illustrate the effect of the Beryllium window on the diffracted x-ray beam.

The automation of the data taking process on the double crystal spectrometer was described earlier.[16] This arrangement has proven to be quite satisfactory during the past year and has been reported in the literature.[17] A recent improvement has been the use of the PIP-400 in the multiscale mode to record the rocking curve data so that easy comparisons of successive rocking curves can be made. The PIP-400 has three data output options: photograph of cathode ray display, x-y recorder output, and digital readout into a 33ASR Teletype page printer and paper tape punch. For this purpose up to four rocking curves can be stored and overlapped for easy comparison before readout, usually by photograph. The PIP-400 is an option in addition to the regular readout of data through the ORTEC 432 and the other Teletype unit.

III RESULTS

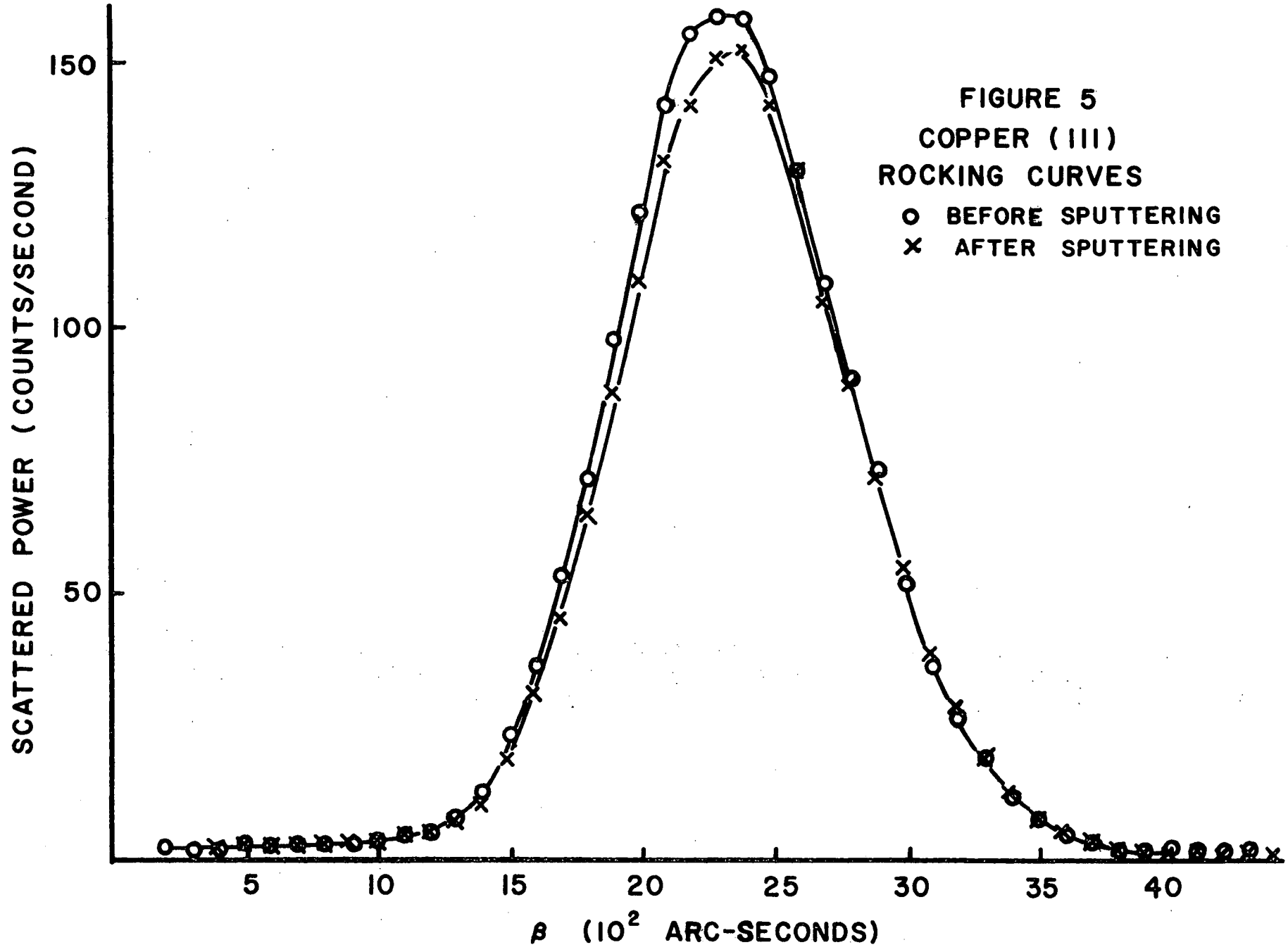
Preliminary data have been obtained on both copper and germanium crystals. These crystals have been through a sputtering and annealing sequence along with the appropriate rocking curves. The crystal has been placed in the twelve inch vacuum chamber approximately four inches away from the ion gun. After sputtering the crystal is removed from the vacuum chamber and placed in the standard sample holder on the double crystal spectrometer. The crystal orientation in the sample is carefully preserved from one rocking curve to the next by using lines on the crystal edge and surface gauge pointers.


SCATTERED POWER (10^4 COUNTS/SECOND)
1
2
3
4
5
6
2
4
6
8
10
12
14
16
18
20
22
ARC-SECONDS
FIGURE 4
QUARTZ (200)
ROCKING CURVES
CRYSTAL IN CHAMBER
CRYSTAL OUT OF CHAMBER

The copper single crystals[8] were grown by the Czochralski technique, polished, strain annealed, and oriented to (111). The matched crystal technique[18] is used for these studies. Crystal A, the crystal nearest the x-ray tube, is selected so that its lattice planes are as parallel as possible to the planes of crystal B, the crystal to be analyzed. For copper (111) in crystal B, a quartz crystal in the (200) reflection is used in position A. This combination not only has a close match on lattice spacings (2.081Å for copper vs 2.128 Å for quartz) but also the width of the quartz rocking curve (~4 sec) is much narrower than the copper rocking curve (1100 sec) which makes the curve separation problem much simpler.[19]

Figure 5 shows the copper (111) rocking curve before and after sputtering with 1500 V Argon ions for 15 hours at 50 μA, a dose of about 3 Coulombs for the one inch diameter crystal. Only part of the crystal face was in the ion beam but rocking curves in the two regions were the same. During this rocking curve and sputtering sequence, the copper crystal was observed to take on a double-peaked appearance as shown in Figure 6. Many tests were performed to check the spectrometer and crystals to determine the cause of the double peak. When it was finally determined that the crystals were producing the effect and not the spectrometer the crystal supplier was contacted. Apparently crystals grown with this technique sometimes undergo slippage. The amount of slippage for the copper crystal was found to be about 40 minutes of arc. Venetron now offers crystals grown by the Bridgeman technique and four new copper crystals have recently been obtained.

By using a narrow beam so that only a very small region of the copper crystals were examined it was possible to continue using the old copper crystals during delivery of the new ones. Annealing the copper crystal at 750°C for thirty minutes produced no change in the rocking curve.


150
100
50
SCATTERED POWER (COUNTS/SECOND)
5
10
15
20
25
30
35
40
β (10² ARC-SECONDS)
FIGURE 5
COPPER (111)
ROCKING CURVES
BEFORE SPUTTERING
AFTER SPUTTERING

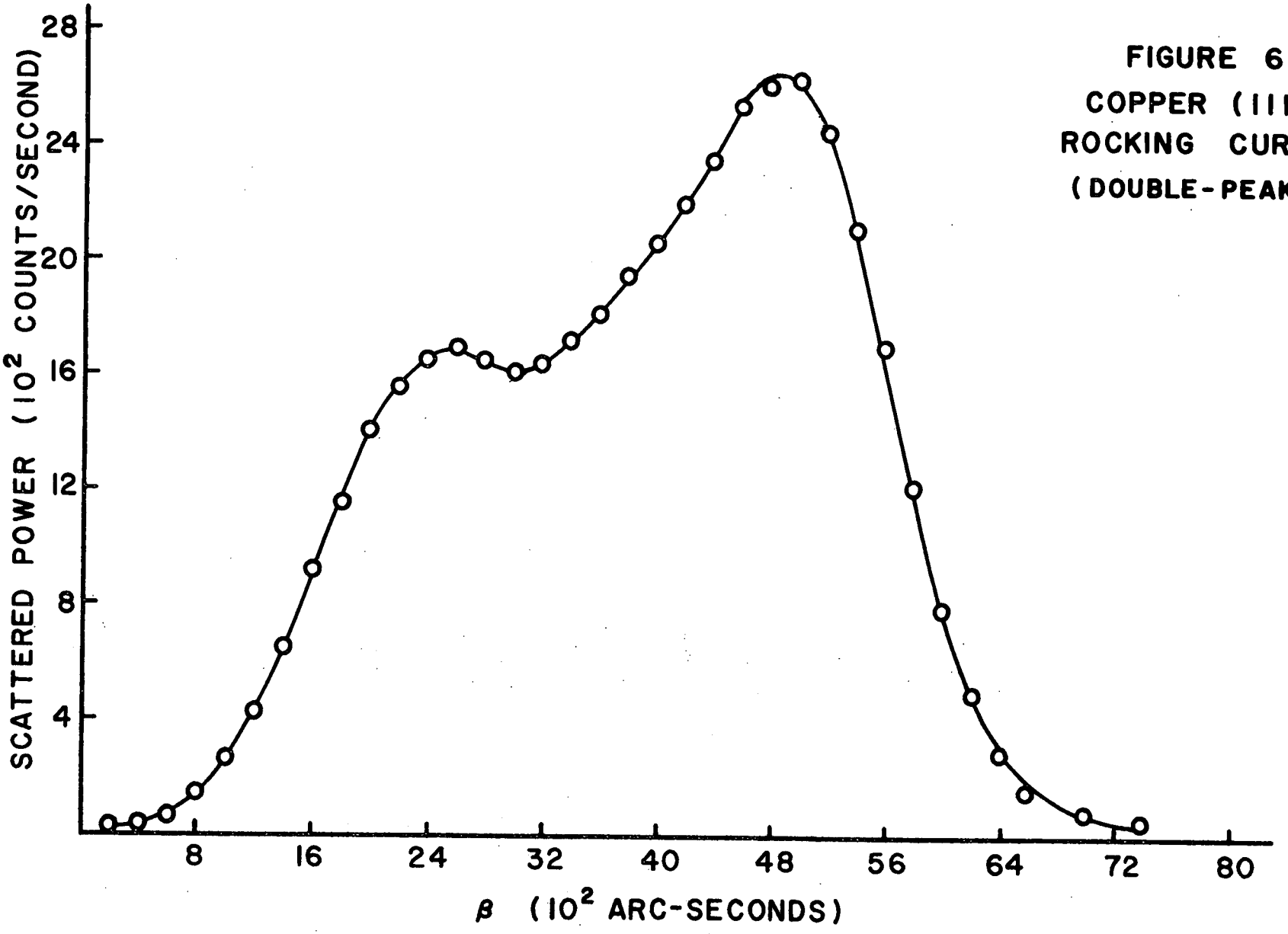


FIGURE 6
COPPER (111)
ROCKING CURVE
(DOUBLE-PEAKED)

TABLE 3

Preliminary Damage Studies of Germanium

PROCESS	COMMENTS	HALF WIDTH
Rocking Curve		22.2 sec
Sputter	1.0 Coulombs	
Rocking Curve		21.6 sec
Anneal	100 minutes at above 450°C	
Rocking Curve		22.4
Sputter	2.5 Coulombs	
Rocking Curve		21.4
Sputter	1.2 Coulombs	
Rocking Curve		21.8

The germanium single crystals were also grown by the Czochralski technique.[8] They were one inch in diameter by one-quarter inch thick, polished, strain annealed, and oriented to (111). No quartz reflection spacing was found to be useful for use with the germanium crystal to utilize the matched crystal technique so a second germanium crystal was used as crystal A. The sputtering, annealing, and rocking curve sequence is summarized in Table 3 above. There appears to be no apparent increase in half width of the rocking curve for germanium with a fairly severe dose of ion bombardment.

Recent work on low energy ion bombardment damage in germanium[20] indicates that with 1000 V Argon ions the damage effects saturated with an ion dose of 1×10^{17} ions/cm^2. In addition the damage should penetrate approximately 25 layers, i.e. 50 Å. The dosage attained at Hiram College was 2.5×10^{19} ions/cm^2 for 2.0 Coulomb dose over the face of the 1" diameter crystal assuming singly charged ions. Due to room temperature fluctuation the precision of the half width measurement is ± 0.3 sec as determined from taking a series of rocking curves without repositioning

the crystal. Attempts to reduce the temperature effect on the spectrometer precision will continue but since the spectrometer is automated to minimum step sizes of 0.5 sec and the mechanical precision of the micrometer is only good to 0.2 sec the above value of 0.3 sec is probably about as good as can be expected.

IV RECOMMENDATIONS AND PROBLEMS

In spite of the difficulties to date, eg. delayed delivery of custom equipment, lack of local machine shop facilities for repair, etc., a fairly effective x-ray research program has been developed and set up at Hiram College. The equipment is now all apparently operational and the main problem is enough time to complete more of the proposed work. The research schedule is now about where it should have been last year at this time. Performing such a research task at a small college has been a learning experience in management techniques as essentially all fabrication of equipment must be done elsewhere with the attendant delays, necessary modifications, and, sometimes modifications due to the item not meeting specifications. However, the research program has been of great benefit to Hiram College since the involvement of undergraduate students working in close cooperation with faculty members on a significant research problem has contributed to the enhancement of the students' professional careers.

The preliminary data on copper and germanium apparently show that the expected line broadening due to ion damage is less than the precision of the measurement and possibly unmeasureably small. However, the data needs more analysis particularly in the tail region of the rocking curves. Adequate computer time has been a slight problem this summer so much of the data is still being processed. The damage study in the new copper crystals will begin next as will a renewed effort at obtaining double crystal topographs as a possibly more sensitive method of determining ion bombardment damage.

V REFERENCES

1. Varian Associates, Palo Alto, California.

2. L. B. Shaffer, "Defect Production in Single Crystals Resulting from Ion Bombardment," Semi-Annual Status Report #4, August 9, 1968, NASA Grant NGR 36-019-001.

3. L. B. Shaffer, "Defect Production in Single Crystals Resulting from Ion Bombardment," Semi-Annual Status Reports #3 and 4, NASA Grant NGR 36-019-001.

4. Trademark of Varian Associates, Palo Alto, California.

5. Heath Company, Benton Harbor, Michigan, Catalog No. EUW-20A.

6. Air Products and Chemicals Inc., Allentown, Pennsylvania.

7. Varian Associates, Palo Alto, California, Catalog No. 951-5100.

8. Venetron Electronics Corporation, Bradford, Pennsylvania.

9. L. B. Shaffer, "Defect Production in Single Crystals Resulting from Ion Bombardment," Semi-Annual Status Report #4, August 9, 1968, NASA Grant NGR 36-019-001.

10. L. B. Shaffer, "Defect Production in Single Crystals Resulting from Ion Bombardment," Semi-Annual Status Report #4, August 9, 1968, NASA Grant NGR 36-019-001.

11. L. B. Shaffer, "Defect Production in Single Crystals Resulting from Ion Bombardment," Semi-Annual Status Report #2, July 31, 1967, NASA Grant NGR 36-019-001.

12. Enraf-Nonius Inc., Garden City Park, New Jersey, Catalog No. Y601

13. R. D. Deslattes, et,al., J. Appl. Phys., 37, 541(1966).

14. L. B. Shaffer, "Defect Production in Single Crystals Resulting from Ion Bombardment," Semi-Annual Status Report #4, August 9, 1968, NASA Grant NGR 36-019-001, Figure 2.

15. H. W. Schnopper, Ph.D. Thesis (Cornell University, 1962), available from University Microfilms, Inc., Ann Arbor, Michigan, as No. 62-5994.

16. L. B. Shaffer, "Defect Production in Single Crystals Resulting from Ion Bombardment," Semi-Annual Status Report #4, August 9, 1968, NASA Grant NGR 36-019-001.

V REFERENCES

17. D. J. Dorson and L. B. Shaffer, Bull. Am. Phys. Soc. 14, 801 (1969).

18. L. Kaufman and S. A. Kulin, Trans. Amer. Inst. Min. (Metall.) Engrs., 215, 273(1959).

19. A. H. Compton and S. K. Allison, X-Rays in Theory and Experiment, (P. Van Nostrand Company, Inc., New York, 1935), pp. 718.

20. R. J. MacDonald and D. Haneman, J. Appl. Phys. 37, 1609(1966).